Water-Quality Assessment of the Trinity River Basin, Texas—Pesticides in Streams Draining an Urban and an Agricultural Area, 1993–95

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Abstract

Water and bed-sediment samples from streams draining an urban and an agricultural area in the Trinity River Basin, Texas, were analyzed. The samples were collected during March 1993–September 1995 by the Trinity River Basin study-unit team of the National Water-Quality Assessment Program.

A comparison of pesticide data for water samples from seven streams in the Dallas-Fort Worth urban area with five streams in an agricultural area in the west-central part of the Trinity River Basin showed detections of 24 herbicides in urban-area streams and 19 herbicides in agricultural-area streams and 10 insecticides in each area. Atrazine, a herbicide, was detected in all samples from both areas. Diazinon, an insecticide, was detected in all samples collected in urban-area streams and in about 60 percent of the samples collected in agricultural-area streams. Concentrations of alachlor, atrazine, fluometuron, metolachlor, and pendimethalin (herbicides) were always greater in agricultural-area streams, and prometon and simazine concentrations were always greater in urban-area streams. Atrazine was the only herbicide with concentrations greater than a health advisory limit of 3 micrograms per liter. Concentrations were greater in about 20 percent of the samples; all were in the agricultural area and occurred during spring and during higher streamflow. Diazinon was the only insecticide with concentrations greater than the health advisory of 0.6 microgram per liter. Concentrations were greater in about 15 percent of the samples from the urban area. All exceedances were during spring through early fall and during all ranges of streamflow. In the agricultural area, atrazine and metolachlor concentrations peaked during spring and early summer and increased with increasing streamflow; in the urban area, carbaryl, chlorpyrifos, and diazinon peaked in April and remained relatively high during the summer and increased with increasing streamflow.

A comparison of pesticide data for bed-sediment samples from five urban streams and five agricultural streams showed detections of 11 organochlorine insecticides in the urban area and 1 in the agricultural area. All compounds were either DDT-related or one of the components of chlordane except for mirex and dieldrin.

INTRODUCTION

The U.S. Geological Survey (USGS) implemented the National Water-Quality Assessment (NAWQA) Program in 1990 (Leahy and others, 1990) with the following primary objectives:

- Describe the water-quality conditions of many of the Nation's streams and aquifers,
- Define long-term trends in water quality, and
- Identify, describe, and explain, to the extent possible, the major natural and human factors that affect water-quality conditions and trends.

NAWQA has 60 study areas distributed across the Nation that provide building blocks of water-quality information. Consistent plans and protocols allow information from the study areas to be aggregated and studied at the local, State, regional, and national levels. The strategy for implementing the program was to start one-third of the study units in each of the fiscal years 1991, 1994, and 1997. The Trinity River Basin study in Texas (fig. 1) began in 1991.

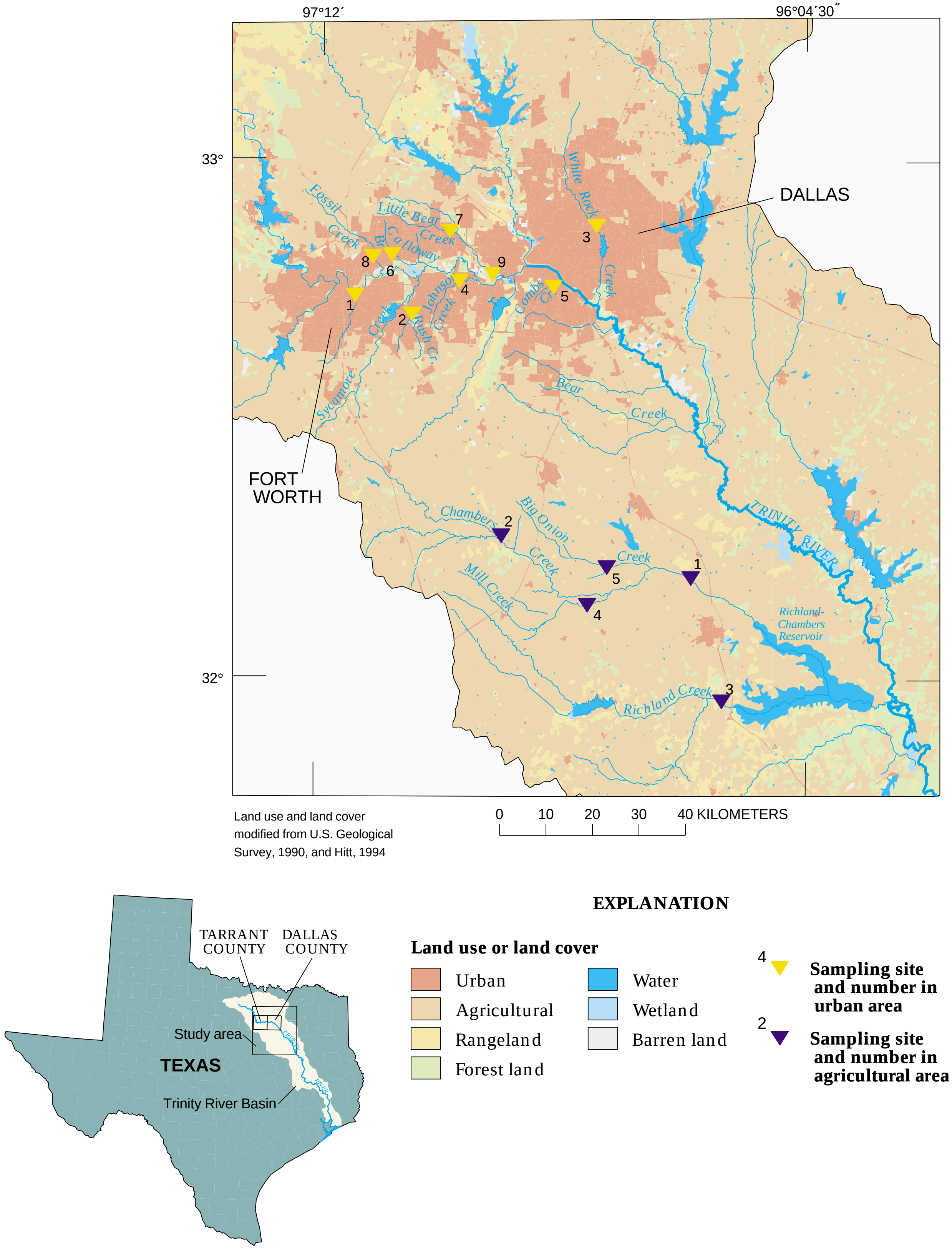

Figure 1. Location of the Trinity River Basin, urban and agricultural areas, and data-collection sites.

NAWQA’s approach to water-quality assessment of streams is to (1) measure the physical properties and chemical constituents of water, (2) measure trace elements and hydrophobic organic contaminants in bed sediment and organisms, and (3) characterize aquatic communities and habitat. This approach provides "multiple lines" of data to define and characterize water-quality conditions and to provide a baseline definition for determining changes and trends. All data are collected from networks of 8 to 12 sites within each study area. Some of the stream sites represent watersheds with rather uniform environmental settings, and others, generally on the main stem of the river, represent complex parts of the basin where there are a variety of point- and nonpoint-source contaminants and environmental settings. In watersheds that have numerous sources of contaminants, temporal variability is defined by frequent sampling during seasons when contaminants such as fertilizers and pesticides are most available and storm runoff could transport them to the streams. In addition, spatial variations during selected seasons and hydrologic conditions are defined by synoptic surveys. Finally, temporal and spatial variability in local areas are assessed by special studies.

Water-quality issues in the area were identified by a liaison committee comprising representatives from Federal, State, and local agencies and others who have water-resources responsibilities and expertise. Although contamination of streams by pesticides has not been documented in the basin, nonpoint-source contaminants in urban and agricultural streams are one of the major water-quality issues identified by the liaison committee. To study this issue, the study-unit team grouped the consistent water-quality data collected from several networks into two data sets for comparison and statistical analyses. One data set includes sites in the Dallas-Fort Worth metropolitan area, and the other includes sites in the watersheds of Richland Creek and Chambers Creek, which are in one of the most intensively farmed areas in the Trinity River Basin.

Purpose and Scope

The primary purpose of this report is to improve the understanding of nonpoint-source pesticide contamination of streams draining urban and agricultural watersheds. More specifically, the purposes are to compare the pesticides in streams draining an urban area and an agricultural area by showing the distributions of pesticide concentrations and how the concentrations vary with seasons and streamflow, and to explain, to a limited extent, any patterns. The scope of the report is limited to water and bed-sediment samples for pesticide analyses collected by the NAWQA study-unit team during March 1993–September 1995 at sites in the Dallas-Fort Worth metropolitan area and in the Richland Creek and Chambers Creek watersheds. The pesticides of concern are herbicides and insecticides in water and organochlorine insecticides in bed sediments.

Description of Study Areas and Pesticide Uses

The study-unit team collected samples in two study areas (fig. 1). One is in the Dallas-Fort Worth metropolitan (urban) area in Dallas and Tarrant Counties where more than 3.5 million people lived in 1990 (Hitt, 1994). The other is a rural (agricultural) area in the west-central part of the Trinity River Basin where fertile soils are extensively cultivated. The sampling sites are shown on figure 1.

In the urban area, only sites without major point sources such as municipal wastewater plants or major industrial plants in the watershed were considered. For the purposes of this study, seven stream monitoring sites had a sufficient number of water samples and five sites had suitable bed-sediment samples (table 1). The seven sites where water samples were collected are in watersheds with drainage areas between 13 and 174 km^2. Land use in these watersheds is primarily urban. Urban land use consists of residential areas (more than 50 percent), commercial areas such as shopping centers and office complexes along major highways and streets (1 to 30 percent), and industrial and other urban land uses (less than 5 percent). The average population density in the urban area is about 650 people per 1 km^2. Two other sites in the urban area where only bed-sediment samples were collected are in watersheds with relatively large drainage areas. Land use in these watersheds consists of urban (32 and 43 percent) and other uses, such as agriculture.

Selective herbicides commonly are used in the urban area by residents, business owners, and municipal workers to kill or prevent weeds in lawns. Nonselective herbicides are used to control all plants in limited areas along streets and highways, especially around signs, culverts, and bridges, and also are used by residents and others in some landscape settings. According to a national survey of home pesticide use (Whitmore and others, 1992), herbicides commonly applied by homeowners include 2,4–D, acifluorfen, atrazine, dicamba,

Table 1. Location and description of sampling sites in an urban and an agricultural area in the Trinity River Basin, Texas

Sampling site no. (fig. 1)	U.S. Geological Survey station or identification no.	Stream	Water samples collected	Bed-sediment samples collected	Drainage area (square kilometers)	Land use (percent)[1]		
						Urban	Agricultural	Other
		Urban area						
1	08048542	Sycamore Creek	x	x	75	83	17	0
2	08049240	Rush Creek	x	x	70	66	29	5
3	08057200	White Rock Creek	x	x	174	70	29	1
4	324407097052499	Johnson Creek	x		18	95	5	0
5	324546096503399	Combs Creek	x		13	98	0	2
6	324851097115399	Calloway Branch	x		18	100	0	0
7	325147097040599	Little Bear Creek	x		60	64	32	4
8	324724096581698	Bear Creek		x	231	43	48	9
9	324853097151498	Fossil Creek		x	148	32	67	1
		Agricultural area						
1	08064100	Chambers Creek	x	x	2,150	3	92	5
2	3214410096442601	Chambers Creek	x	x	850	2	92	6
3	315801096282999	Richland Creek	x	x	1,920	1	87	12
4	321017096420099	Mill Creek	x	x	241	2	98	0
5	321313096415201	Big Onion Creek	x	x	150	.5	97	2.5

[1] Hitt, 1994.

oryzalin, prometon, triclopyr, and trifluralin. Atrazine, prometon, and triclopyr probably do not have as much home use in the Dallas-Fort Worth area as was indicated in the national survey (Mike Merchant, Texas Agricultural Extension Service, oral commun., 1996). Herbicides such as 2,4–D, dicamba, oryzalin, and simazine typically are used by municipalities. Professional lawn-care companies reported using dicamba, MCPA, and simazine. There is little information on the quantities of the herbicides applied or the timing of their applications. One noted exception is that the lawn-care companies use different herbicides during different seasons—dicamba and MCPA in the spring and simazine in the fall. Some of the herbicides commonly used in the urban area but not included in NAWQA laboratory analyses are glyphosate, MCPP, mecoprop, MSMA, and oxyfluorfen.

Insecticides are used most often in the urban area to control insects in and near residences, businesses, golf courses, and parks. Many of these pests are a problem in spring when rain is more frequent and temperatures are moderate. However, other pests such as fire ants are a problem throughout the year. Insecticides are used extensively in the urban area for control of termites around buildings. Insecticides heavily used by homeowners include carbaryl, chlorpyrifos, diazinon, and malathion (Whitmore and others, 1992; and Mike Merchant, Texas Agricultural Extension Service, oral commun., 1996). Carbaryl, chlorpyrifos, and diazinon also are used by lawn-care companies and municipalities. Other commonly used insecticides not included in NAWQA laboratory analyses are acephate, pyrethrins, and pyrethroids such as permethrin, which is used on lawns and gardens and for termite control.

In the agricultural area, water and bed-sediment samples for pesticide analyses were collected at five stream monitoring sites (table 1). Three sites are in watersheds with drainage areas between 150 and 850 km^2. The two remaining sites are in watersheds with much larger drainage areas, greater than 1,900 km^2. Numerous reservoirs built in the area control about 25 percent of the drainage area upstream of Richland-Chambers Reservoir. The land use is primarily agricultural, consisting mostly of cropland and pasture with some rangeland. In cultivated areas, major crops are corn, cotton, sorghum, and hay. Some pecans and oats also are grown. None of the crops is irrigated. In pasture and rangeland areas, cattle are the dominant livestock.

In the agricultural area, herbicides often are applied to the soil in late winter or early spring before planting major crops. They are applied again, as needed, during the growing season, especially the early part. On the basis of estimated pesticide use for the area, atrazine is used on corn and in combination with metolachlor on corn and sorghum (Bill Harris, Texas Agricultural Extension Service, written commun., 1991). Metolachlor also is used independently on corn, cotton, and sorghum. Corn also can be treated with alachlor. Cotton is treated with several other herbicides, including fluometuron and trifluralin; herbicides used on cotton but not included in NAWQA laboratory analyses are glyphosate, MSMA, and prometryn. Cotton also is treated with defoliants. Arsenic acid commonly was used for this purpose through 1994 but has been replaced primarily by paraquat. Herbicides such as 2,4–D and picloram are used in much smaller amounts on hay fields but not at all on rangeland. Herbicides are applied around residences, businesses, and along highways similar to that described for urban areas.

Selected insecticides are used in the agricultural area to control insects that inflict major damage to crops, especially corn and cotton. These chemicals are applied in the late spring and early summer as necessary. The Texas Agricultural Extension Service estimates were used to identify commonly used insecticides for the area. Corn is treated with terbufos. Ethyl parathion is used on cotton, oats, and wheat; and methyl parathion is used on cotton and oats. Cotton also is treated with aldicarb, propargyte, and thiodicarb. Carbofuran is used on sorghum; dimethoate is used on pecans and wheat; and carbaryl is used on several minor crops such as hay, oats, pecans, and rye. Nonagricultural insecticide use in the area is similar to that described for the urban area.

METHODS OF DATA COLLECTION AND ANALYSES

Sampling Networks

Data collected from several Trinity River Basin NAWQA networks were aggregated and analyzed for this investigation. One of the networks consists of two sites where pesticide samples were collected repeatedly to provide a seasonal definition of concentrations in streams. One site (USGS station 08049240) is in a suburban watershed between Dallas and Fort Worth that is drained by Rush Creek. The second site (USGS station 08064100) is in a watershed drained by Chambers Creek, where corn, cotton, and sorghum are produced. Several other networks provided sites where pesticide samples were collected. The NAWQA program stresses the use of common protocols for sample collection and processing and for laboratory analyses, thereby allowing data from any of the networks to be aggregated and compared.

Data Collection and Laboratory Analyses

All samples for data presented in this report were collected between March 1993 and September 1995. Sampling was concentrated during the spring and early summer when most of the pesticides are applied and when there are more frequent rainstorms to transport them to the streams. Data for pesticides in water are presented only for sites with six or more samples. Composited-width and -depth samples were collected using field-sampling techniques for water (Shelton, 1994). Following NAWQA protocols to prevent contamination and constituent degradation, the samples were immediately processed and preserved in the field. Finally, the samples were taken to the field office or express mailed to the laboratory for immediate extraction of the constituents. Two laboratory procedures were used. One procedure extracts the pesticides onto a C–18 solid-phase cartridge, analyzes the extract with gas chromatography (GC), and detects the compounds with mass spectrometry (MS) (M.W. Sandstrom and others, USGS National Water Quality Laboratory, written commun., 1993). The other procedure extracts the pesticides onto a Carbopak–B solid-phase extraction cartridge, analyzes the extract with high performance liquid chromatography (HPLC), and detects the compounds with ultraviolet spectroscopy (UV) (M.R. Burkhardt and S.L. Werner, USGS National Water Quality Laboratory, written commun., 1993). Together, the procedures determined concentrations of about 80 pesticides. The method detection limits for these pesticides range between 0.004 and 0.05 μg/L (S.R. Glodt, USGS National Water Quality Laboratory, written commun., 1994). However, the laboratory analyst often records a substantially lower concentration as an estimated value. When this was the case, the estimated value was entered into the data base and used in this study. Other laboratory analyses for water samples included major inorganic ions, nutrients, organic carbon, and sediment. Field measurements comprised stream discharge, specific conductance, pH, water temperature, and dissolved oxygen.

Quality-assurance and quality-control (QA/QC) procedures included submitting to the laboratory (1) blank samples (organic free water) to detect any contamination between the stream and final laboratory analyses and (2) duplicate samples. About 15 percent of all field samples were QA/QC samples. Pesticides were not detected in any of the field blank samples. A review of the duplicate-sample data indicates that the concentration of a given sample is usually within 10 percent, often much less, of concentrations of other samples except for samples with very low concentrations.

Composited samples of surficial fine-grained material were collected using field-sampling techniques for bed-sediment samples (Shelton and Capel, 1994). The samples were wet sieved in the field to produce a sample with particle sizes of 2.0 mm or less. In the laboratory, the pesticides were extracted by Soxhlet and analyzed by dual capillary-column GC with electron-capture detection (E.T. Furlong and others, USGS National Water Quality Laboratory, written commun., 1993). The method detection limits range between 1.0 and 5.0 μg/kg. Other laboratory analyses for bed-sediment samples comprised trace elements, semivolatile organic compounds, and grain-size distribution.

QA/QC procedures included submitting a duplicate sample for every 5 to 10 bed-sediment samples. The results of the QA/QC data for bed-sediment samples show that the concentration of a given sample usually is within 10 percent of concentrations of other samples except for samples with very low concentrations.

Statistical Analyses

Statistical analyses of the pesticide data determine differences or similarities between urban-area data and agricultural-area data and identify seasonal patterns and relation to streamflow. Three techniques were used to analyze the data. Two of the techniques are nonparametric, two-sample tests to evaluate differences between the urban-area data set and the agricultural-area data set. The third technique graphically relates the data sets to season and to streamflow.

The Wilcoxon signed-rank test, which determines if the median difference between paired observations equals zero (Helsel and Hirsch, 1992), was used to compare the percent detections of pesticides in samples from the urban area to those from the agricultural area. The percent detections for a pesticide indicate how frequently it was detected in the samples collected and is a measure of its occurrence in the streams. The Wilcoxon signed-rank test produces a statistic from matched pairs of data that identifies at a given confidence level (95 percent in this study) whether there is a significant difference between two independent data sets.

A similar test, the Peto-Prentice score test for nonparametric, two-sample data sets (Helsel and Malacane, in press), was used to identify significant differences between pesticide concentrations detected in the two areas. This score test is more appropriate than a signed-rank test for statistical analysis of concentration data because the score test compares two data sets that have multiple method detection limits without censoring the data to the highest limit. Concentration data were compared only for those pesticides detected in an average (for the two areas) of 20 percent or more of the samples.

The third technique calculates a smooth line from a scatterplot to graphically show the relation of each of the pesticide-concentration data sets to season and to streamflow. The LOcally WEighted Scatterplot Smoothing (LOWESS) line (Cleveland, 1979, *in* Helsel and Hirsch, 1992) is a statistical procedure to construct a resistant centerline on an x–y scatterplot to highlight trends or patterns in the data. Because concentrations near the center of the data have greater influence on the LOWESS line than concentrations farther away, the effect of outliers on the pattern is minimized. In calculating the smooth line, a concentration reported as a less-than value was set to this value.

Table 2. Results of Wilcoxon signed-rank test to determine if percent detections of pesticides in water samples are significantly different between urban- and agricultural-area streams in the Trinity River Basin, Texas, 1993–95

Pesticide	p-value[1]	Result at 95-percent confidence level		
		Urban greater than agricultural	No difference	Agricultural greater than urban
Herbicides	0.07		x	
Insecticides	.06		x	

[1] The p-value is the "attained significance level" derived from the data in a statistical test. It is the probability of getting the computed test statistic under the assumption that the data being compared (urban-area data and agricultural-area data in this report) are not different. "Not different" in this context means that the data come from the same population.

PESTICIDES IN STREAMS DRAINING AN URBAN AND AN AGRICULTURAL AREA

The water and bed-sediment samples collected by the Trinity River Basin NAWQA study-unit team between March 1993 and September 1995 were grouped into one data set representing urban-area streams and one data set representing agricultural-area streams. The results of the pesticide analyses are presented separately for water samples and for bed-sediment samples.

Herbicides and Insecticides in Water

The water samples were compared to determine (1) the occurrence of herbicides and insecticides and (2) the variability of herbicide and insecticide concentrations by season and with streamflow.

Pesticides Detected

The detection of a pesticide in a sample can be referred to as an occurrence. The frequency of occurrence for a pesticide can be expressed as the percent detected in the total number of samples. The percent detections of pesticides in water samples from urban- and agricultural-area streams are shown on figure 2. Each group of herbicides and insecticides is listed by decreasing frequency of detection.

Of the 24 herbicides detected in urban-area streams and the 19 detected in agricultural-area streams, 15 herbicides were detected in both areas. Atrazine, the most commonly detected, occurred in all samples from both areas. Metolachlor occurred in about 80 percent of the samples from urban-area streams and in all samples from agricultural-area streams. According to Texas Agricultural Extension Service estimates, atrazine and metolachlor are two of the most extensively applied herbicides in the agricultural area (Bill Harris, Texas Agricultural Extension Service, written commun., 1991). Atrazine is also in some products used for home lawn care. Atrazine and metolachlor also have been detected in air and rain samples in other studies, indicating the possibility of atmospheric deposition (Majewski and Capel, 1995). Two other commonly detected herbicides, prometon and simazine, occurred in about 90 percent of the urban-area samples and in about 60 percent of the agricultural-area samples. Both herbicides are used in non-cropland areas. Except for the cotton herbicide fluometuron, which was not detected in urban-area samples but was detected in about 60 percent of agricultural-area samples, all remaining detected herbicides occurred in less than 50 percent of the samples from either area. Despite the differences in detections for individual compounds, the Wilcoxon signed-rank test indicates that for this group of herbicides, there is no significant difference between percent detections in urban-area streams and those in agricultural-area streams (table 2). However, it should be noted that the p-value is 0.07; a result of 0.05 would indicate a significant difference.

Ten insecticides were detected in urban-area streams and nine in agricultural-area streams (fig. 2). The frequency of detections was much greater in the urban area, with three insecticides occurring in more than 50 percent of the samples. In the agricultural area, only one insecticide was detected in more than 50 percent of the samples—diazinon occurred in all samples from urban-area streams and in about 60 percent of the samples from agricultural-area streams. Diazinon has the highest number of outdoor applications for insecticides according to the national survey of home pesticide use (Whitmore and others, 1992) and is one of the most

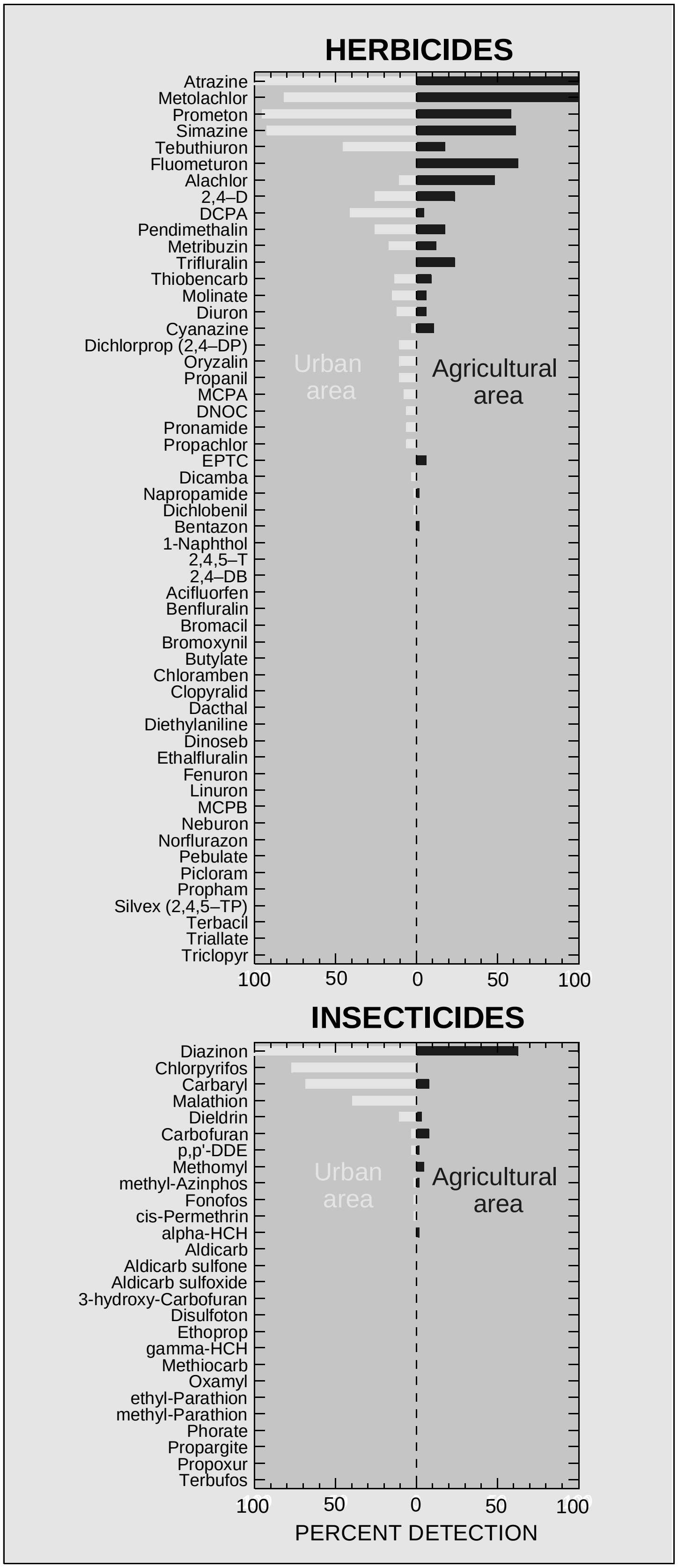

Figure 2. Detections of pesticides in streams draining an urban and an agricultural area in the Trinity River Basin, Texas, 1993–95.

frequently used home insecticides in the Dallas-Fort Worth area (Mike Merchant, Texas Agricultural Extension Service, oral commun., 1996). Like atrazine and metolachlor, diazinon has been detected in air and rain samples in other studies (Majewski and Capel, 1995). The two other most frequently detected insecticides in the urban area, chlorpyrifos and carbaryl, also are rated among the pesticides with the highest number of outdoor applications according to the national home survey and are used frequently in the study area. Other than diazinon, all insecticides detected in the agricultural area occurred in less than 10 percent of the samples. Based on the Wilcoxon signed-rank test, there is no significant difference between percent detections of this group of insecticides in urban-area streams and those in agricultural-area streams (table 2) despite differences in individual compounds. Again the p-value of 0.06 is very near 0.05, which would indicate a significant difference.

Comparing the most commonly applied pesticides with the most commonly detected ones produced some anomalies. Metolachlor is not listed by homeowners as a widely used herbicide in the urban area but was detected in about 80 percent of the samples. The high percent detections of metolachlor could be caused by (1) the possible atmospheric deposition from use in agricultural areas and (2) its stability in water, even in the presence of sunlight—only 6.6 percent degrading in 30 days (U.S. Environmental Protection Agency, 1980). Tebuthiuron and DCPA were detected in 40 to 50 percent of the urban-area samples but are not listed among the compounds applied by homeowners, lawn-care companies, and municipalities. However, tebuthiuron is associated with weed control in industrial areas and could have substantial use that is not known. Prometon and simazine are not among the highly used agricultural herbicides but occurred in about 60 percent of the samples from the agricultural area. The reasons for the large number of detections have not been determined but might be related to nonagricultural uses or to properties and environmental fate characteristics of the compounds.

Concentrations of Commonly Detected Pesticides

In addition to determining which pesticides are occurring in the streams, it is important to measure concentrations. To illustrate the distribution of concentrations and to compare the concentrations in the urban and agricultural areas, the most commonly detected herbicides and the most commonly detected insecticides were graphed in percentile plots (fig. 3). The 10 herbicides and 4 insecticides were selected for graphing on the basis of an average (for the two areas) of at least 20-percent detections. Each concentration of the selected pesticides above the method detection limit was plotted against the percent of concentrations that were less than or equal to that concentration. For example, a concentration plotted at the 0 percentile is the minimum concentration; the 50 percentile is the median concentration; and the 100 percentile is the maximum concentration. The graphs of herbicides show that alachlor, atrazine, fluometuron, and metolachlor concentrations were greater in samples from agricultural-area streams and that pendimethalin, prometon, and simazine concentrations were greater in samples from urban-area streams. This is generally consistent with pesticide uses in the urban and agricultural areas. The distributions of 2,4–D, DCPA, and tebuthiuron concentrations were similar for the two areas.

Three herbicides—2,4–D, atrazine, and metolachlor—were detected at a concentration of 1.0 μg/L or greater in at least one sample from both areas. Two herbicides—alachlor and fluometuron—were detected at a concentration of 1.0 μg/L or greater in at least one sample from the agricultural area. Atrazine was the most frequently detected herbicide and had the greatest concentrations for both areas.

The distributions of the four most frequently detected insecticides show that the concentrations were greater in all samples from urban-area streams than in samples from agricultural-area streams (fig. 3). Carbaryl and diazinon concentrations are 1.0 μg/L or greater in at least one sample from urban-area streams. These two insecticides commonly are applied in the urban area. No insecticides were detected at concentrations of 1.0 μg/L or greater in agricultural-area streams.

The Peto-Prentice score test was used to determine if there is a significant difference between concentrations of the 10 herbicides and 4 insecticides in water samples from urban-area streams and concentrations in samples from agricultural-area streams. Concentrations of four herbicides were significantly greater in urban-area streams than in agricultural-area streams, and concentrations of four other herbicides were significantly greater in agricultural-area streams than in urban-area streams (table 3). Concentrations of the four insecticides were significantly greater in urban-area streams than in agricultural-area streams.

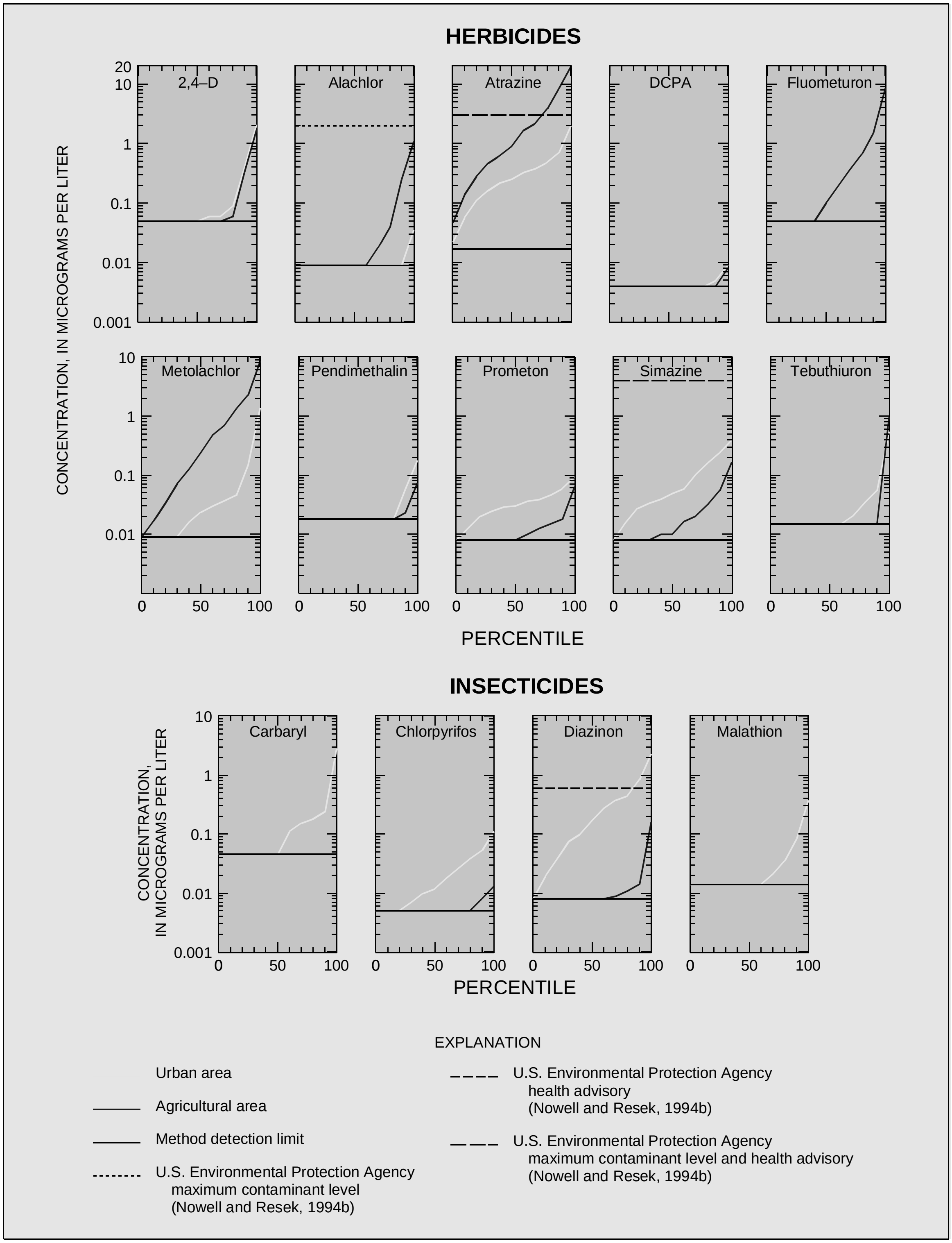

Figure 3. Distribution of concentrations above the method detection limit of fourteen most commonly detected pesticides in streams draining an urban and an agricultural area in the Trinity River Basin, Texas, 1993–95.

Table 3. Results of Peto-Prentice score test to determine if pesticide concentrations in water samples are significantly different between urban- and agricultural-area streams in the Trinity River Basin, Texas, 1993–95

Pesticide	p-value[1]	Result at 95-percent confidence level: Urban greater than agricultural	Result at 95-percent confidence level: No difference	Result at 95-percent confidence level: Agricultural greater than urban
		Herbicides		
2,4–D	0.57		x	
Alachlor	<.01			x
Atrazine	<.01			x
DCPA	<.01	x		
Fluometuron	<.01			x
Metolachlor	<.01			x
Pendimethalin	.98		x	
Prometon	<.01	x		
Simazine	<.01	x		
Tebuthiuron	<.01	x		
		Insecticides		
Carbaryl	<.01	x		
Chlorpyrifos	<.01	x		
Diazinon	<.01	x		
Malathion	<.01	x		

[1] The p-value is the "attained significance level" derived from the data in a statistical test. It is the probability of getting the computed test statistic under the assumption that the data being compared (urban-area data and agricultural-area data in this

Comparison of pesticide concentrations to available water-quality standards (table 4) puts the concentrations in perspective in terms of potential health risks. As quantitative methods improve, pesticides might be detected at concentrations well below the levels that substantially affect the ecosystem or human health. The U.S. Environmental Protection Agency (USEPA) maximum contaminant level (MCL) is the maximum permissible level of a contaminant in water delivered to any user of a public water system. The USEPA health advisory (HA) is the nonregulatory level of a contaminant in drinking water that can be used for guidance in the absence of regulatory limits. The HAs listed in table 4 were established for an individual's lifetime (70 years) exposure to drinking water to provide protection against adverse health effects not related to cancer and are based on a body weight of 70 kg and consumption of 2 L/d of drinking water (Nowell and Resek, 1994a). Ambient water-quality standards for the protection of aquatic organisms are not listed in the table because they have been determined for few of the pesticides compared in this analysis.

Atrazine was the only herbicide with concentrations greater than the MCL and HA (3 µg/L, table 4). Atrazine concentrations in about 20 percent of the samples from agricultural-area streams were greater (fig. 3). Diazinon was the only insecticide with concentrations greater than the HA (0.6 µg/L, table 4). Diazinon concentrations in about 15 percent of the samples from urban-area streams were greater (fig. 3). Only the applicable water-quality standards within the range of the plots are shown on figure 3.

Seasonal concentrations of pesticides detected in urban- and agricultural-area streams were determined and compared. Seasonal variability (seasonality) is shown by graphing the concentrations of the most

Table 4. Selected water-quality standards for pesticides in water

[MCL, maximum contaminant level; HA, health advisory; --, not available]

Pesticide	U.S. Environmental Protection Agency MCL (micrograms per liter)[1]	U.S. Environmental Protection Agency HA (micrograms per liter)[1]
2,4–D	70	70
Alachlor	2	--
Atrazine	3	3
Carbaryl	--	700
Chlorpyrifos	--	20
DCPA	--	4,000
Diazinon	--	.6
Fluometuron	--	90
Malathion	--	100
Metolachlor	--	100
Prometon	--	100
Simazine	4	4
Tebuthiuron	--	500

[1] Nowell and Resek, 1994b.

commonly detected herbicides (fig. 4) and the most commonly detected insecticides (fig. 5) versus the date regardless of year. For example, concentrations plotted for March could have been sampled in March 1993, 1994, or 1995. Only those pesticides detected in at least 50 percent of the samples from either area and with concentrations above method detection limits in both areas (four herbicides and three insecticides) were chosen for analysis.

The seasonality plots for herbicide concentrations (fig. 4) show a great amount of scatter for both areas. During March through June, when most of the samples were collected, the high concentration often was nearly 10 times greater than the low concentration for both urban- and agricultural-area streams. The LOWESS lines for herbicides (fig. 4) show that, throughout the year, prometon and simazine concentrations tended to be greater in urban-area streams while atrazine and metolachlor concentrations tended to be greater in agricultural-area streams. In terms of seasonality, atrazine and metolachlor concentrations were greater during spring and early summer. The seasonality was more pronounced and the concentrations were greater in agricultural-area streams than in urban-area streams. The LOWESS lines show atrazine and metolachlor concentrations tended to peak in April and to have considerable variability throughout the year. During April, the median concentrations of atrazine and metolachlor were 0.8 and 0.04 µg/L, respectively, in the urban-area streams, which is considerably less than the median concentrations of 6.0 and 1.6 µg/L in the agricultural-area streams. During September–January, when concentrations tend to be lowest, median concentrations of atrazine and metolachlor were 0.06 µg/L and less than the method detection limit in the urban-area streams and 0.53 and 0.03 µg/L in the agricultural-area streams. All agricultural-area atrazine concentrations that exceeded the MCL and HA of 3 µg/L occurred between late February and late May. On the basis of the LOWESS lines, prometon concentrations showed essentially no seasonality in either area and had a median concentration of 0.03 µg/L in the urban-area streams and 0.006 µg/L in the agricultural-area streams. Simazine concentrations exhibit rather irregular LOWESS line patterns, with higher concentrations during January to April for both areas. During this

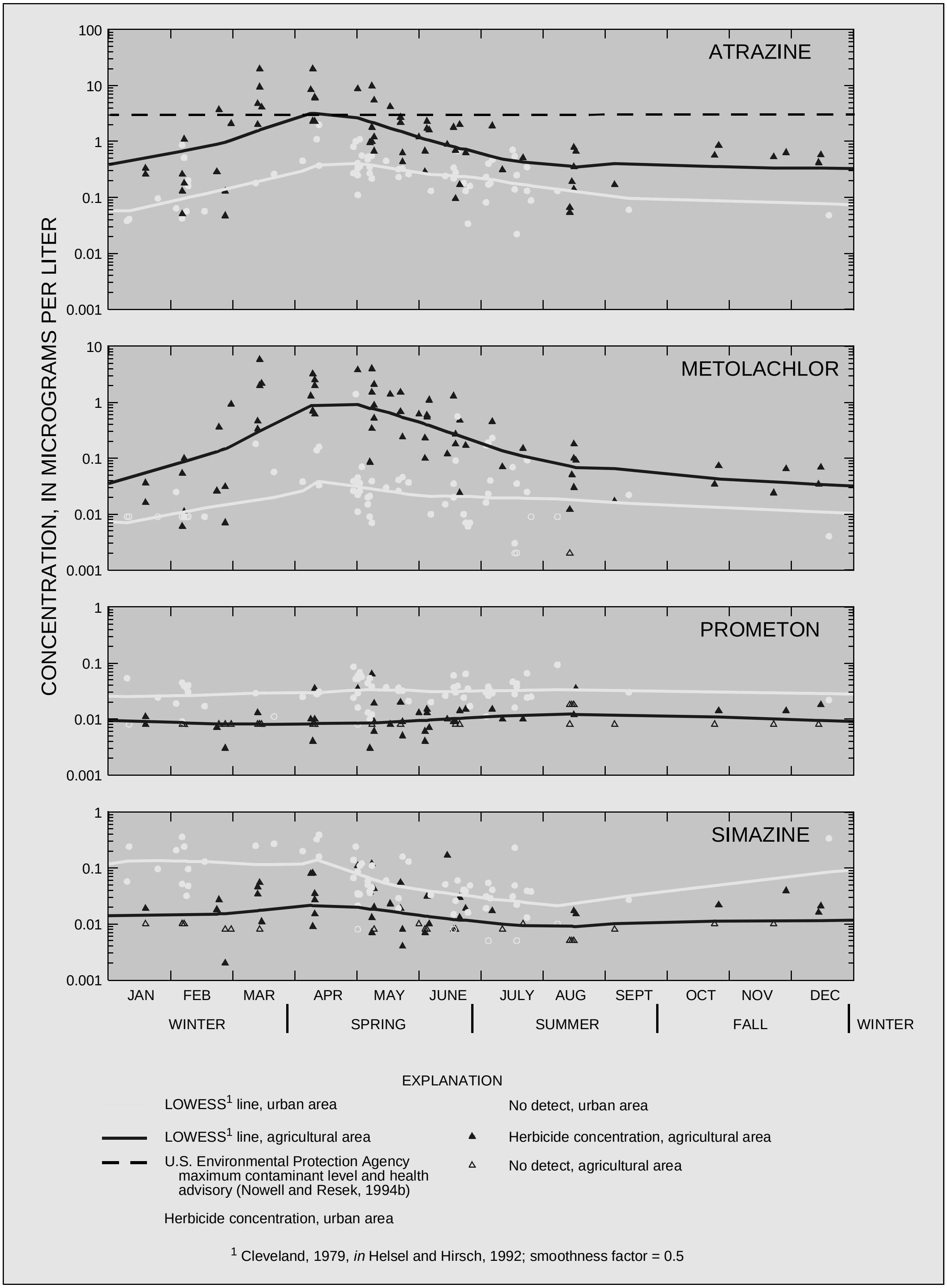

Figure 4. Seasonal variability of concentrations of selected herbicides in streams draining an urban and an agricultural area in the Trinity River Basin, Texas, 1993–95.

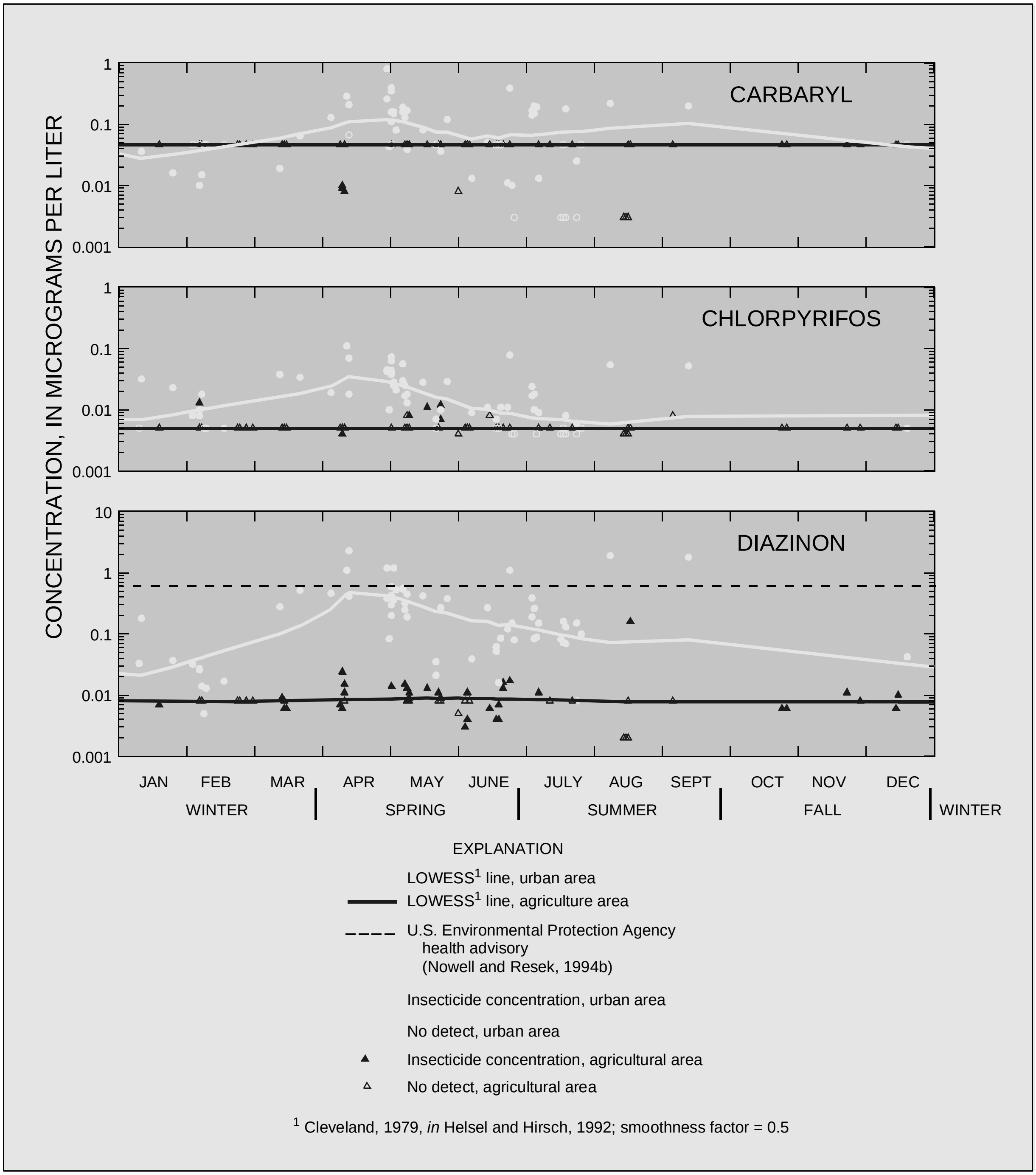

Figure 5. Seasonal variability of concentrations of selected insecticides in streams draining an urban and an agricultural area in the Trinity River Basin, Texas, 1993–95.

period, the median concentration of simazine was 0.18 μg/L in the urban-area streams and less than the method detection limit in the agricultural-area streams. Unlike the three other herbicides, the LOWESS lines of simazine concentrations were lowest during August for both areas.

The seasonality plots for insecticide concentrations (fig. 5) show a great amount of scatter in urban-area streams. In spring, high concentrations often were 10 to 50 times greater than low concentrations. The LOWESS lines for carbaryl, chlorpyrifos, and diazinon in urban-area streams (fig. 5) show concentrations were seasonally greatest in April and remained relatively high through summer. During April, the median concentrations were 0.21, 0.04, and 0.46 µg/L for carbaryl, chlorpyrifos, and diazinon, respectively. As indicated by the LOWESS line, concentrations of these insecticides tend to be lowest during July–February. During this period, the median concentrations were 0.012, 0.007, and 0.08 µg/L, respectively. Urban-area diazinon concentrations exceeding the 0.6-µg/L HA occurred between April and mid-September. Insecticide concentrations in agricultural-area streams show less scatter because detections were uncommon except for diazinon. Most insecticide detections in agricultural-area streams were at or near the method detection limit, thus, no seasonality was evident.

Pesticide concentrations might be elevated during spring and early summer in response to the time of the year when most of the chemicals are applied and when rains are more common and in amounts great enough to cause runoff. However, not all the pesticides respond the same way to this process. The pesticides with greater concentrations (atrazine, metolachlor, and diazinon) showed the greatest seasonality. Except for metolachlor in urban areas, these pesticides are probably in greatest use. The lack of seasonality for prometon and simazine could indicate rather low use of the pesticides and the stream response of concentrations remaining near background levels throughout the year; or, it could indicate use of the pesticides throughout the year.

The variability of pesticide concentrations with streamflow is shown by graphing concentrations of the four most commonly detected herbicides and the three most commonly detected insecticides versus unit discharge at the time of sampling (figs. 6 and 7). Unit discharge (discharge divided by drainage area, referred to as streamflow), in cubic meters per second per square kilometer, was used to adjust for the difference in drainage areas among the sites.

The plots of herbicide concentrations against unit discharge (fig. 6) show a great amount of scatter in both areas. The range between low and high concentrations often was greater than a factor of 10. The LOWESS lines for herbicides show atrazine and metolachlor concentrations tended to be greater in agricultural-area streams than in urban-area streams throughout the range in streamflow. The opposite occurred for prometon and simazine. The LOWESS lines of atrazine and metolachlor concentrations in both areas were rather uniform below about 0.001 $(m^3/s)/km^2$; above this streamflow, agricultural-area streams showed increasing concentrations with streamflow while urban-area streams showed a gradual increase in concentrations up to about 0.007 $(m^3/s)/km^2$ followed by a gradual decrease in concentrations. For streamflow less than 0.001 $(m^3/s)/km^2$, the median concentrations of atrazine and metolachlor were 0.16 and 0.01 µg/L, respectively, in the urban-area streams, somewhat less than the median concentrations of 0.28 and 0.06 µg/L in the agricultural-area streams. For streamflow greater than 0.1 $(m^3/s)/km^2$, the median concentrations of atrazine and metolachlor increased to 0.53 and 0.015 µg/L in the urban-area streams and 3.2 and 0.92 µg/L in the agricultural-area streams. All agricultural atrazine concentrations greater than the HA of 3 µg/L occurred at unit discharges greater than 0.004 $(m^3/s)/km^2$. The LOWESS line for simazine in urban-area streams shows concentrations were rather uniform from low flow to high flow except for higher concentrations in the 0.001- to 0.01-$(m^3/s)/km^2$ range where the median concentration was 0.08 µg/L. The LOWESS line for simazine in agricultural-area streams shows concentrations generally were low below 0.002 $(m^3/s)/km^2$ and increased with increasing streamflow where the median concentration was 0.04 µg/L above 0.1 $(m^3/s)/km^2$. The LOWESS lines for prometon show concentrations in both areas were rather uniform throughout the range in streamflow with the urban-area streams having a median concentration of 0.03 µg/L, and the agricultural-area streams having a median concentration of 0.006 µg/L.

The plots of insecticide concentrations versus unit discharge (fig. 7) show a large degree of scatter (a factor of 10 or more) in urban-area streams, but less in agricultural-area streams because most of the concentrations were at or near method detection limits. LOWESS lines for insecticides in urban-area streams (fig. 7) show that concentrations of carbaryl, chlorpyrifos, and diazinon gradually increased above a unit discharge of 0.001 $(m^3/s)/km^2$, while concentrations in agricultural-area streams remained near method detection limits. For streamflow less than 0.001 $(m^3/s)/km^2$ in urban-area streams, the concentrations of carbaryl and chlorpyrifos are at or near the method detection limits and the median concentration of diazinon was 0.07 µg/L. For high flows [greater than 0.1 $(m^3/s)/km^2$], the median concentrations increase to 0.19, 0.03, and 0.54 µg/L for carbaryl, chlorpyrifos, and diazinon,

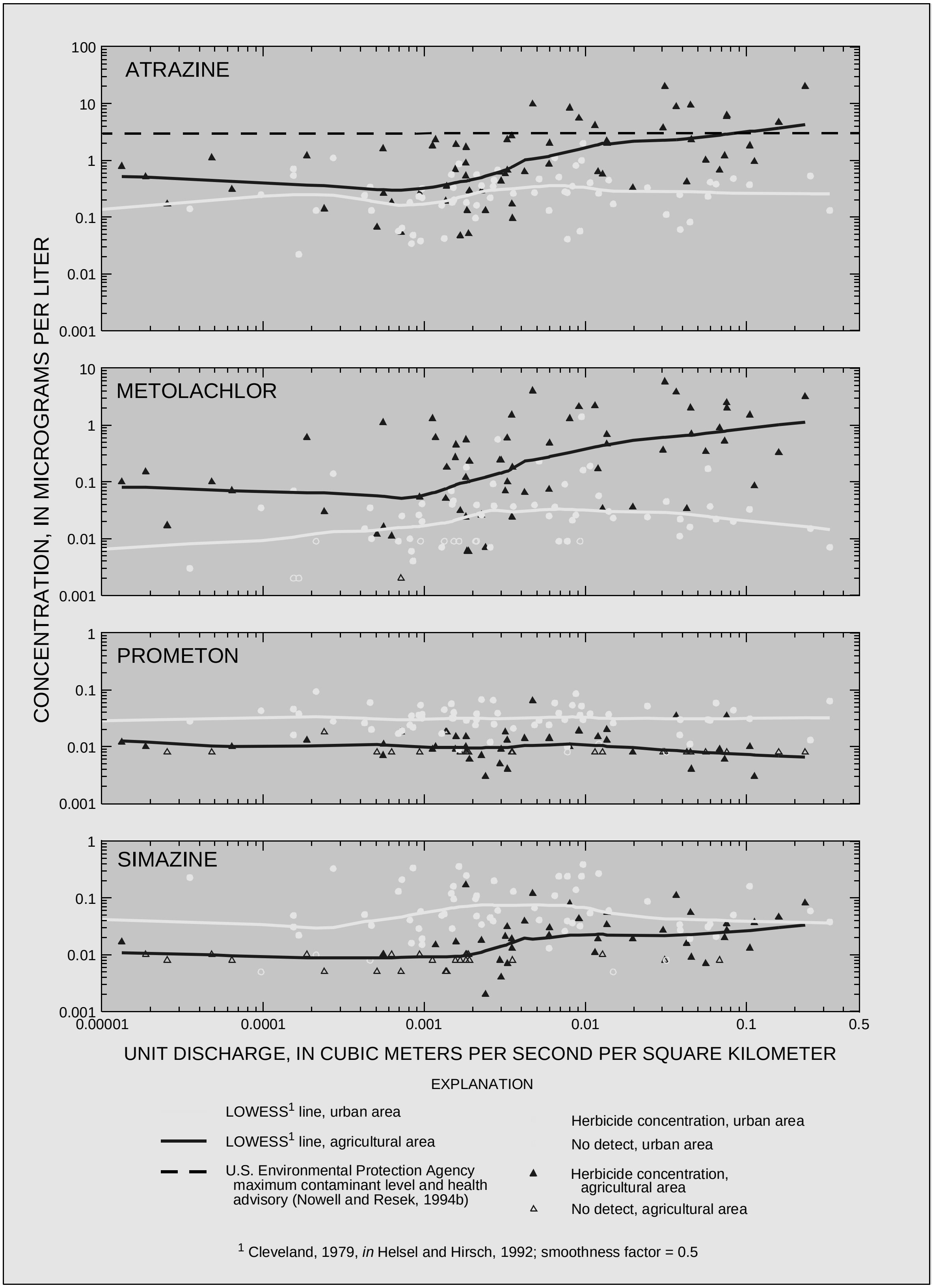

Figure 6. Variability of concentrations of selected herbicides with streamflow in an urban and an agricultural area in the Trinity River Basin, Texas, 1993–95.

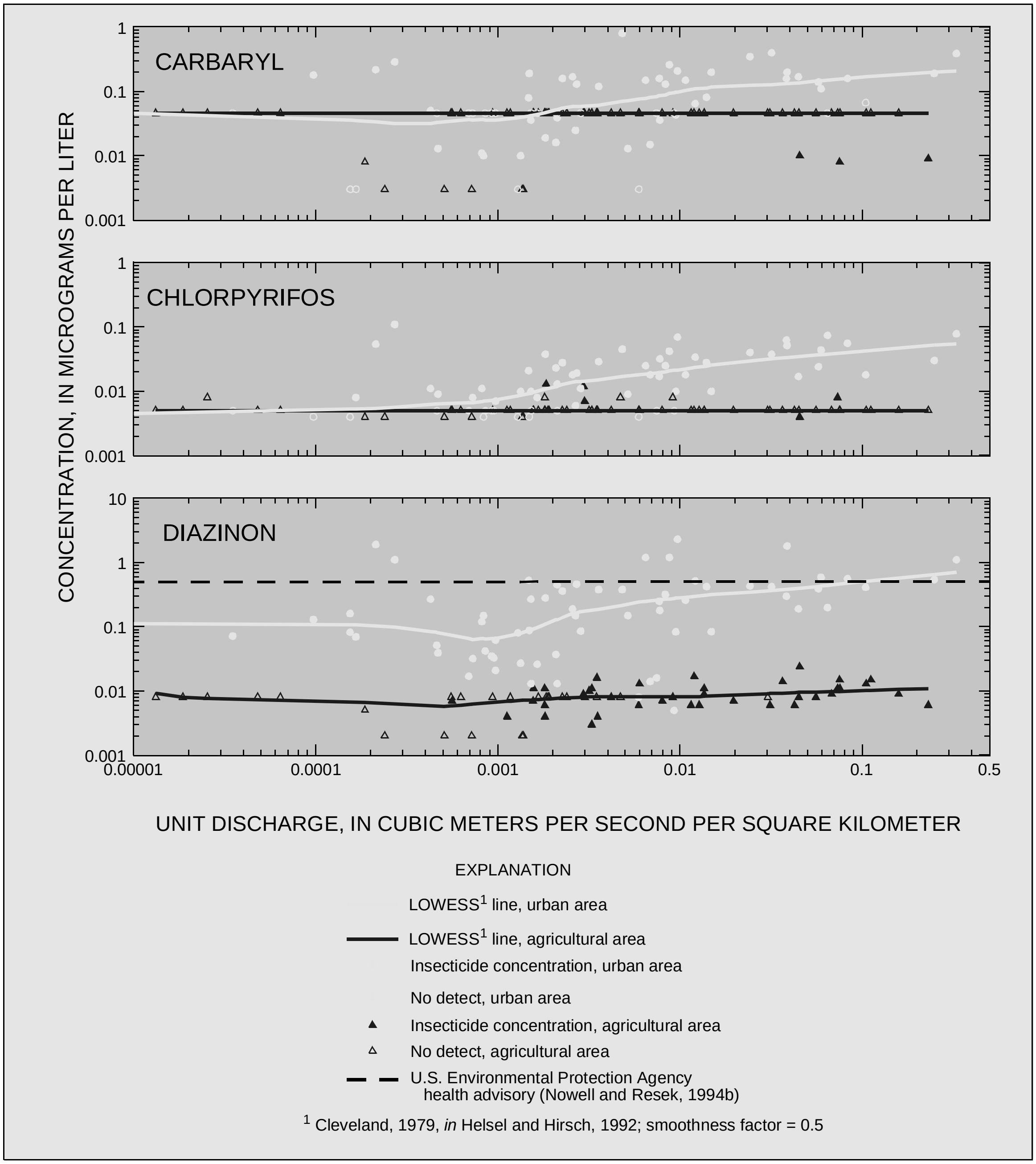

Figure 7. Variability of concentrations of selected insecticides with streamflow in an urban and an agricultural area in the Trinity River Basin, Texas, 1993-95.

respectively. Diazinon concentrations greater than the 0.6-µg/L HA occurred throughout the range of streamflow in the urban area.

Two phenomena are evident in the relation between pesticide concentration and streamflow. One—increasing concentration with increasing streamflow—might represent a readily available constituent in the watershed that is being washed off in proportion to the amount of excess rainfall (runoff) or might represent reduced time of floodflows to transport compounds between an area of application and point of sampling, providing less time for the compound to degrade. The second phenomenon—decreasing concentration with increasing streamflow—might represent dilution of a

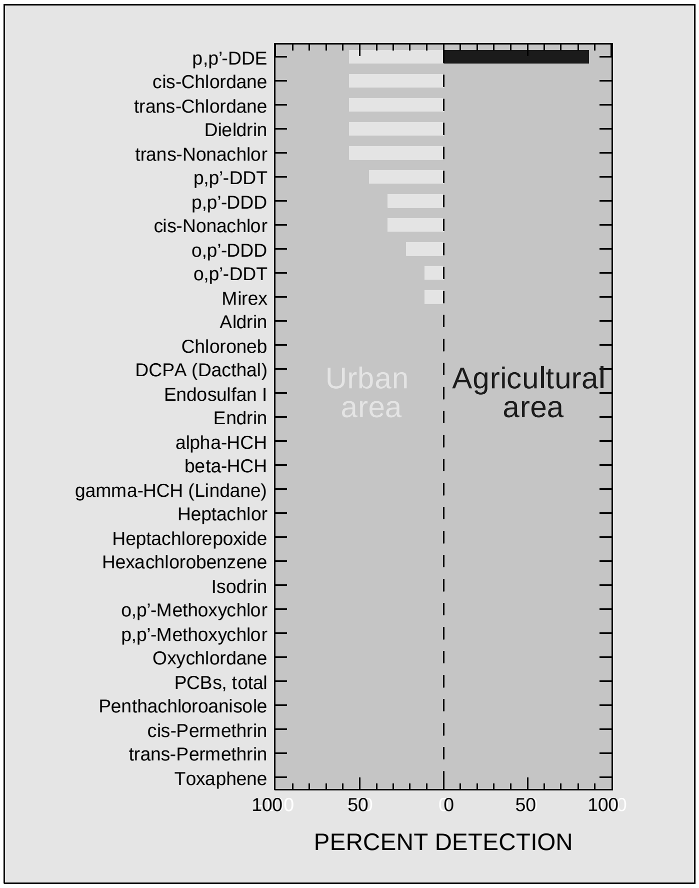

Figure 8. Detections of organochlorine insecticides in bed sediments of streams draining an urban and an agricultural area in the Trinity River Basin, Texas, 1993–95.

limited or fixed source of a constituent. The graphs (figs. 6 and 7) might indicate an availability of atrazine, metolachlor, and simazine in the agricultural area and of carbaryl, chlorpyrifos, and diazinon in the urban area. Availability of the other pesticides in the watersheds was considered to be limited because concentrations remain about the same through all ranges of streamflow.

Insecticides in Bed Sediments

The accumulation of organochlorine insecticides is the most common issue associated with pesticides in bed sediments. This type of insecticide is hydrophobic and persistent in the environment despite discontinued application. The data were analyzed to identify which of these insecticides are detected and to determine the differences between occurrences and concentrations in bed-sediment samples from urban-area streams and occurrences and concentrations in bed-sediment samples from agricultural-area streams.

Insecticides Detected

Eleven insecticides were detected in bed-sediment samples from urban-area streams, and one insecticide was detected in bed-sediment samples from agricultural-area streams (fig. 8). With the exception of mirex, used for fire ant control, and dieldrin, all detected insecticides were either DDT-related compounds (DDT, DDE, DDD) or components of chlordane (forms of chlordane and nonachlor), which formerly was used extensively to control termites. On the basis of the Wilcoxon signed-rank test, the percent detections of insecticides in bed-sediment samples from urban-area streams were significantly greater than percent detections in bed-sediment samples from agricultural-area streams ($p = 0.01$). The only insecticide detected in both areas was *p,p'*-DDE.

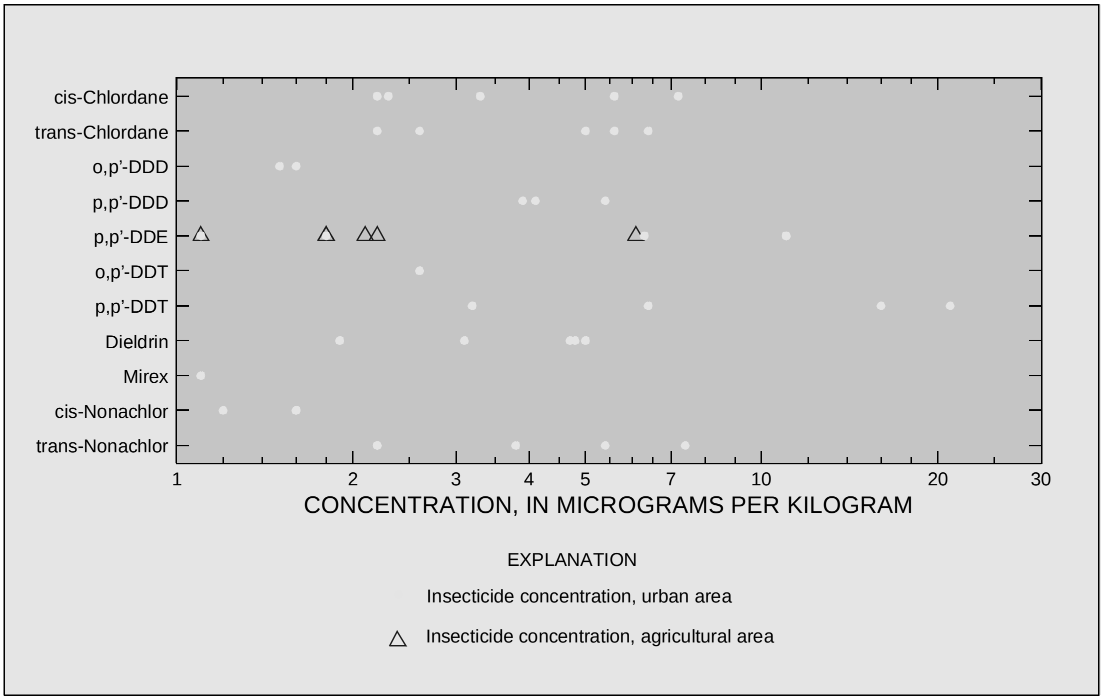

Figure 9. Distribution of concentrations of organochlorine insecticides detected in bed sediments of streams draining an urban and an agricultural area in the Trinity River Basin, Texas, 1993–95.

Concentrations of Commonly Detected Insecticides

The USEPA interim, tentative, and draft sediment-quality criteria (SQC) are the only standards available for pesticides in bed sediment. These criteria, when finalized, will constitute the USEPA recommendation for pesticide concentrations in sediment that will not have an unacceptable effect on benthic organisms (Nowell and Resek, 1994a). These criteria are given in terms of mass of pesticide per mass of sediment organic carbon. These preliminary standards are available only for chlordane and *p,p'*-DDT; the proposed standards are well above any of the concentrations detected in bed-sediment samples from urban- or agricultural-area streams during this study.

The pesticide concentrations from the two areas can be compared statistically and graphically. Because sediments accumulate over time, no sampling was done for seasonality or relation to streamflow.

The Peto-Prentice score test identifies significant differences between insecticide concentrations in the two areas (table 5). Because this score test uses "less than" values for no detects, the results indicate those organochlorine insecticides that had enough detections in the urban area for those concentrations, as a group, to be significantly greater than the no detects in the agricultural area. Concentrations of *cis*-chlordane, *trans*-chlordane, *trans*-nonachlor, *p,p'*-DDT, and dieldrin were significantly greater in bed-sediment samples from urban-area streams.

The distribution of insecticide concentrations (fig. 9) shows insecticides were detected much more often and at greater concentrations in bed-sediment samples from urban-area streams than in samples from agricultural-area streams. Most concentrations in samples from urban-area streams were less than 8.0 µg/kg except for *p,p'*-DDE and *p,p'*-DDT, which were as much as 11 and 21 µg/kg, respectively. Concentrations in agricultural-area streams were less than 7 µg/kg.

The statistical and graphical comparisons of organochlorine insecticides and metabolites in bed-sediment samples from urban- and agricultural-area streams indicate much greater historical use of the insecticides in the urban area. Furthermore, their persistence in the environment is indicated despite discontinued use. Another possible explanation is the dilution of the insecticides in sediment by the relatively large amount of erosion in agricultural areas in comparison to urban areas.

Table 5. Results of Peto-Prentice score test to determine if organochlorine insecticide concentrations in bed-sediment samples are significantly different between urban- and agricultural-area streams in the Trinity River Basin, Texas, 1993–95

Organochlorine insecticide	p-value[1]	Result at 95-percent confidence level		
		Urban greater than agricultural	No difference	Agricultural greater than urban
cis-Chlordane	0.02	x		
trans-Chlordane	.02	x		
o,p'-DDD	.23		x	
p,p'-DDD	.20		x	
p,p'-DDE	.64		x	
o,p'-DDT	.41		x	
p,p'-DDT	.05	x		
Dieldrin	.02	x		
Mirex	.41		x	
cis-Nonachlor	.10		x	
trans-Nonachlor	.02	x		

[1] The p-value is the "attained significance level" derived from the data in a statistical test. It is the probability of getting the computed test statistic under the assumption that the data being compared (urban-area data and agricultural-area data in

SUMMARY

Results from analyses of pesticides in water and bed-sediment samples collected during March 1993–September 1995 from streams draining urban and agricultural areas in the Trinity River Basin, Texas, are summarized below:

Which pesticides were detected?

- Of the 24 herbicides detected in water samples from urban-area streams and the 19 detected in water samples from agricultural-area streams, 15 herbicides were detected in both areas. Atrazine, the most commonly detected, occurred in all samples from both areas.

- Ten insecticides were detected in water samples from urban-area streams and ten in water samples from agricultural-area streams. The frequency of detections was much greater in the urban area. Diazinon, the most commonly detected, occurred in all samples from urban-area streams and in about 60 percent of the samples from agricultural-area streams.

- Metolachlor is not listed as a widely used herbicide in the urban area but occurred in about 80 percent of the water samples from urban-area streams. Prometon and simazine are not among the highly used agricultural herbicides but occurred in about 60 percent of the water samples from agricultural-area streams.

What were the pesticide concentrations?

- Concentrations of the herbicides alachlor, atrazine, fluometuron, and metolachlor in water samples were always greater in agricultural-area streams, and concentrations of pendimethalin, prometon, and simazine were always greater in urban-area streams.

- Concentrations of insecticides were always greater in water samples from urban-area streams than from agricultural-area streams.

- Atrazine was the only herbicide with concentrations in water samples greater than the applicable water-quality standards. About 20 percent of the atrazine concentrations in agricultural-area streams were greater than the MCL and HA of 3 μg/L.

- Diazinon was the only insecticide with concentrations in water samples greater than the HA of 0.6 μg/L. About 15 percent of the diazinon concentrations in urban-area streams were greater.

When were pesticides detected?

- Atrazine and metolachlor concentrations in water samples from both areas were greater during spring and early summer and peaked in April. The seasonality was more pronounced and the concentrations were greater in agricultural-area streams than in urban-area streams.

- Atrazine peaked in April at about 0.4 μg/L for urban-area streams and at about 4 μg/L for agricultural-area streams.

- Atrazine had a baseline concentration during fall and winter of about 0.05 μg/L in urban-area streams and 0.3 μg/L in agricultural-area streams.

- Concentrations of carbaryl, chlorpyrifos, and diazinon in water samples from urban-area streams were seasonally greatest in April and remained relatively high throughout the summer. Most concentrations of these insecticides in water samples from agricultural-area streams were at or near method detection limits, thus indicating no seasonality.

- Higher pesticide concentrations in water samples during spring and early summer might be in response to the time of the year when most chemicals are applied and when rains are more common and in amounts great enough to cause runoff. Greater seasonality was indicated for pesticides with greater concentrations—atrazine, metolachlor, and diazinon. The lack of seasonality for prometon and simazine concentrations might be in response to fairly low use of the pesticides, and thus, concentrations in streams remain near background levels throughout the year, or it could be in response to more constant usage throughout the year.

What was the relation of pesticides to streamflow?

- Atrazine and metolachlor concentrations in water samples were always greater throughout the range of streamflow in agricultural-area streams, and simazine and prometon concentrations were always greater in urban-area streams. All atrazine concentrations in agricultural-area streams greater than the 3-μg/L MCL and HA occurred at streamflow greater than 0.004 $(m^3/s)/km^2$.

- Increasing pesticide concentrations with increasing streamflow could indicate a readily available source of atrazine, metolachlor, and simazine in agricultural-area streams and readily available carbaryl, chlorpyrifos, and diazinon in urban-area streams. Another possibility is that there is less time for the pesticides to break down before reaching the stream sampling site because higher rates of runoff produce shorter transit times. Decreasing pesticide concentrations with increasing streamflow could indicate a limited availability of pesticides in the watersheds because concentrations remain near background levels through all ranges of streamflow.

Which insecticides were detected in bed sediment and what were the concentrations?

- Eleven organochlorine insecticides were detected in bed-sediment samples from urban-area streams and one was detected in bed-sediment samples from agricultural-area streams.

- All insecticides detected in bed-sediment samples, with the exception of mirex and dieldrin, were either DDT-related compounds or one of the components of chlordane.

- Insecticide concentrations in bed-sediment samples from urban-area streams were less than 8.0 μg/kg except for *p,p'*-DDE and *p,p'*-DDT which were as much as 11 and 21 μg/kg, respectively. Insecticide concentrations in bed-sediment samples from agricultural-area streams were less than 7 μg/kg. These findings could indicate much greater historical use in the urban area of these organochlorine insecticides and their persistence in the environment.

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